[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reaction of Silver Nitrite with Primary Alkyl Halides[1,2]

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A simple procedure is described whereby the reaction of silver nitrite with primary, straight chain, halides routinely gives 73–83% yields of *pure* nitroparaffins. Branching in the vicinity of the reactive site impedes the reaction and in the limiting case of neopentyl iodide no reaction whatsoever occurs. The yields of alkyl nitrites produced when the various halides are treated with silver nitrite have been determined.

In 1872 Meyer and Stuber reported that on refluxing a mixture of amyl iodide and silver nitrite they obtained the corresponding nitrite ester and nitroparaffin.[4] Other examples were soon forthcoming and the reaction, as expressed by equation 1, came to be regarded as a general one

$$RX + AgNO_2 \longrightarrow R{-}NO_2 + R{-}ONO \quad (1)$$

While this reaction has been employed by numerous investigators for the preparation of aliphatic nitro compounds and has, in fact, been studied for its own sake,[5] the literature on this subject is still in a thoroughly confused state. It has, for example, never been established what yields of pure nitro compounds may be expected from various types of alkyl halides. Nor is there any agreement as to how the reaction ought to be carried out for the preparation of pure nitroparaffins.[6]

Our interest in this reaction is twofold: (1) to establish, in a definitive way, how useful it is for the preparation of different kinds of pure aliphatic and alicyclic nitro compounds, and (2) to elucidate the mechanism. The present paper deals primarily with the first of these objectives. However, because of its bearing on the matter of mechanism, the yields of alkyl nitrites have also been determined.

The reaction of silver nitrite with alkyl halides has usually been conducted in the neighborhood of 80 to 110°. This results in a much more complex set of products than is given by eq. 1. It is interesting to note that until a few years ago the reaction was considered to yield only two products, nitroparaffins and alkyl nitrites. In 1947,[7] however, it was shown that when 2-bromoöctane is treated with silver nitrite 2-nitroöctane, 2-octyl nitrite, 2-octyl nitrite, 2-octanol, 2-octanone and other, unidentified products are formed. Analogous results were obtained with 2-iodobutane.[8] Still more recently it has been found that the reaction of cyclopentyl iodide with silver nitrite gives, in addition to the products to be expected from equation 1, cyclopentyl nitrate.[9]

The incursion of side reactions is not limited to cases in which secondary halides are employed. Thus, Cenker has shown that after a benzene solution of 1-bromoheptane is heated with silver nitrite at *ca.* 85°, pure 1-heptyl nitrate is easily isolated from the reaction mixture.[10]

Because of the complications introduced by operating at elevated temperatures[7–10] it was clear that the reaction of silver nitrite with alkyl halides ought to be conducted at as low a temperature as possible. Consequently, in the present study reaction is initiated at ice temperature and then completed at room temperature. Furthermore, because the reaction is exothermic, diethyl ether is used as a diluent. The present procedure is especially advantageous for the preparation of primary nitro compounds because the formation of nitrate esters is prevented, and thus one is able to by-pass the use of concentrated sulfuric acid which is necessary to free nitroparaffins of nitrate esters.[7]

As shown in Table I, primary straight chain bromides and iodides give excellent yields of nitro compounds[11] whereas primary chlorides are completely inert.[12]

TABLE I

THE REACTION OF STRAIGHT CHAIN HALIDES WITH SILVER NITRITE

Halide	Nitroparaffin, %	Nitrite, %
n-Butyl bromide	73	13[a]
n-Butyl iodide	74	12[a]
n-Hexyl chloride[c]	0	0
n-Hexyl bromide	76	10[a]
n-Hexyl iodide	78	13[a]
n-Heptyl bromide	79	11
n-Heptyl iodide	82	10
n-Octyl chloride[c]	0	0
n-Octyl bromide	80	14
n-Octyl iodide	83	11[b]

[a] Determined spectrophotometrically. [b] Spectrophotometric determination shows 14%. [c] 94 to 95% recovered.

Good yields of nitroparaffins are also obtained with branched chain primary bromides and iodides

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(3) Taken, in part, from the Ph.D. Thesis of B. Taub, Purdue University, June, 1952.

(4) V. Meyer and O. Stuber, *Ber.*, **5**, 203 (1872).

(5) R. B. Reynolds and H. Adkins, THIS JOURNAL, **51**, 279 (1929).

(6) See, for example, R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 749; J. Walker "Chemistry of Carbon Compounds," Vol. IA, E. H. Rodd, Editor, Elsevier Publishing Co., Houston, Texas, 1951, p. 358; F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 2nd Ed., 1951, p. 160; A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Company, New York, N. Y., 1948, p. 305; W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, London, 2nd Edition, 1948, pp. 416–417; C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, pp. 292–293.

(7) N. Kornblum, N. N. Lichtin, J. T. Patton and D. C. Iffland, THIS JOURNAL, **69**, 307 (1947).

(8) N. Kornblum, J. T. Patton and J. B. Nordmann, *ibid.*, **70**, 746 (1948).

(9) Analogous results are obtained with cyclohexyl iodide: N. Kornblum and C. Teitelbaum, *ibid.*, **74**, 3076 (1952).

(10) M. Cenker, Ph.D. Thesis, Purdue University, February, 1949.

(11) It must be emphasized that throughout this paper yields refer to highly purified products.

(12) Even after 24 hours of refluxing in ether solution with silver nitrite the primary chlorides are quantitatively recovered.

in which the branching is β to the carbon holding the halogen. Thus, isoamyl bromide and iodide give 3-methyl-1-nitrobutane in 72 and 78% yield, respectively. However, as shown in Table II, branching α to the carbon holding the halogen has a deleterious effect. The reaction employing isobutyl iodide produces a distinctly inferior yield (55–63%) of nitro compound. And when isobutyl bromide is treated with silver nitrite, even after five days only 37% of the bromide has reacted.[13] Finally, neopentyl iodide is completely unaffected by silver nitrite; after 12 hours at 0° and three days at room temperature, 96% of the neopentyl iodide was recovered.[14]

Table II

The Reaction of Branched-Chain Primary Halides with Silver Nitrite

Halide	Nitroparaffin, %	Nitrite,[c] %
Isobutyl bromide[a]	17–18	12–16
Isobutyl iodide	55–63	17–22
Isoamyl bromide	72	22[d]
Isoamyl iodide	78	16
Neopentyl iodide[b]	0	0

[a] 63% of the isobutyl bromide unreacted. The yields of nitroisobutane and isobutyl nitrite do not take this into account. [b] 96% of the neopentyl iodide recovered. [c] Determined spectrophotometrically. [d] Isolated 19%.

The results of a similar study of the reaction of silver nitrite with secondary and tertiary halides will be forthcoming. Suffice it to say for the present that, with secondary halides, the yields of nitroparaffins are in the vicinity of 15% while with tertiary halides the yields are still lower, being in the range 0 to 5%. There is no question, then, that the reaction of silver nitrite with alkyl halides is really useful only for the synthesis of primary nitroparaffins.

Experimental

Some of the silver nitrite employed was Mallinckrodt; it was used just as received. On a number of occasions the silver nitrite was prepared in the following way: silver nitrate (1 mole, 169.9 g.), dissolved in 500 ml. of distilled water was added in small portions with vigorous shaking to a solution of 76 g. (1.1 moles) of sodium nitrite in 250 ml. of distilled water (all operations were carried out well protected from light) and the mixture was then allowed to stand in the dark for 1 hour. The yellow precipitate was filtered with suction, stirred well in 250 ml. of distilled water, and filtered. This was repeated two more times and then the silver nitrite was dried in a vacuum desiccator over potassium hydroxide pellets; yield 134 g. (86%).

Mallinckrodt Anhydrous Diethyl Ether, Analytical Reagent, was employed throughout.

Rectifications were either carried out with a 20-inch modified Widmer column[15] fitted with a variable take-off head, or with a small (50 cm. × 1 cm.) glass-helices packed column.

The alkyl chlorides were obtained by treating highly purified alcohols with thionyl chloride and rectifying through the Widmer column. The bromides were Eastman products, carefully fractionated before use. Only middle cuts of constant $n^{20}\mathrm{D}$ and b.p. were employed. All the iodides (except neopentyl) were prepared by treating the alcohols with red phosphorus and iodine; they were rectified, and only middle cuts of constant $n^{20}\mathrm{D}$ and b.p. were used. Neopentyl iodide was prepared according to Whitmore, Wittle and Harriman.[16]

The Preparation of 1-Nitroöctane.—This is a typical preparation of a primary nitroparaffin. In a three-necked flask fitted with a stirrer, dropping funnel and reflux condenser protected by a drying tube, were placed 100 g. (0.65 mole) of silver nitrite and 150 ml. of anhydrous ether. The mixture was cooled to 0° by an ice-bath and then, with continuous stirring (in the absence of light) 120 g. (0.5 mole) of *n*-octyl iodide was added over a period of two hours. After addition was complete the mixture was stirred at ice temperature for 24 hours after which the ice bath was removed and the mixture was then stirred at room temperature for 36 hours more. At this time a Beilstein test on the ether solution was negative.

The silver salts were removed by filtration and washed thoroughly with more ether. The combined ether solutions were distilled at atmospheric pressure through a modified Widmer column[15] and the residue remaining after removal of the ether was rectified under reduced pressure.

The first seven fractions were pure 1-octyl nitrite: all boiled at 51° (5 mm.), were pale yellow, and had $n^{20}\mathrm{D}$ 1.4124–1.4125; they totalled 8.43 g. (11% yield). This was followed by a small interfraction weighing 4.65 g. whose b.p. ranged from 56 to 71° (3 mm.); $n^{20}\mathrm{D}$ 1.4154 to 1.4320.[17] Finally, 64.9 g. (83% yield) of 1-nitroöctane was obtained. Although it was collected as nine fractions (all colorless) the b.p. range was 71.5 to 72° (3 mm.); $n^{20}\mathrm{D}$ 1.4321–1.4323. *Anal.* Calcd. for $C_8H_{17}NO_2$: N, 8.80. Found: N, 8.64.

1-Nitroöctane is completely insoluble in water but on shaking with 20% aqueous sodium hydroxide it is converted to a crystalline, colorless sodium salt which dissolves completely on adding enough water to make the solution 10% aqueous base. 1-Nitrohexane and -heptane dissolved completely on shaking with 20% aqueous base.[18] Table III lists the properties of the various nitroparaffins obtained.

Table III

Nitroparaffins Produced by Reaction of Silver Nitrite with Alkyl Halides

Nitro compound	B.p. °C.	B.p. Mm.	$n^{20}\mathrm{D}$	Formula	N Analyses, % Calcd.	N Analyses, % Found
1-Nitrobutane[a]	70	45	1.4105			
1-Nitrohexane	76	10	1.4236	$C_6H_{13}NO_2$	10.68	10.68
1-Nitroheptane[b]	64	3	1.4283			
1-Nitroöctane	72	3	1.4323	$C_8H_{17}NO_2$	8.80	8.64
2-Methyl-1-nitropropane	71	65	1.4069	$C_4H_9NO_2$	13.60	13.72
3-Methyl-1-nitrobutane	72	27	1.4171	$C_5H_{11}NO_2$	11.95	12.18

[a] N. Kornblum and G. E. Graham, This Journal, **73**, 4041 (1951), report b.p. 70° (45 mm.) $n^{20}\mathrm{D}$ 1.4108. [b] M. Cenker, Ph.D. Thesis, Purdue University, 1949, reports b.p. 105° (20 mm.), $n^{20}\mathrm{D}$ 1.4280.

All the alkyl iodides completely react with silver nitrite after 24 hours at 0° followed by 36 ± 12 hours at room temperature except, of course, neopentyl iodide which is inert under these conditions. The straight chain bromides re-

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(13) Although genuine rate data are not at hand, there is no question but that isobutyl bromide reacts with silver nitrite much more slowly than any of the other primary bromides studied.

(14) The inertness of neopentyl iodide under conditions which result in complete reaction when straight chain primary iodides are employed must mean that rearward attack on carbon occurs in the process of replacing halogen by nitro or nitrite groups. Confirmation of this view is provided by the finding that optically active 2-bromoöctane yields 2-nitroöctane and 2-octyl nitrite having the inverted configuration [L. Fishbein, unpublished work, Purdue University]. Furthermore, R. A. Smiley [unpublished work, Purdue University] has found that the 2-octyl nitrite and 2-nitroöctane obtained from active 2-iodooctane are produced with inversion.

(15) M. Smith and H. Adkins, This Journal, **60**, 657 (1938).

(16) F. C. Whitmore, E. L. Wittle and B. R. Harriman, *ibid.*, **61**, 1585 (1939).

(17) In a number of instances this interfraction was shown to consist largely of the alcohol. It is probably formed by hydrolysis of a small portion of the nitrite ester, the requisite water having been picked up by the hygroscopic anhydrous ether.

(18) In some early runs nitroparaffins were found to contain small amounts (*ca.* 1%) of nitrate esters. This was traced to contamination of the silver nitrite by silver nitrate. In case of doubt the silver nitrite should be washed exhaustively with water, or recrystallized from water (ref. 7, footnote 29). A convenient method for detecting as little as 1% alkyl nitrate in a nitroparaffin takes advantage of the characteristic nitrate ester infrared absorption bands at 6.15, 7.85 and 11.6 μ.

quired 24 hours at 0° followed by 48 ± 12 hours at room temperature for complete reaction. With isoamyl bromide the reaction was run at 0° for 12 hours and then for 4 days at room temperature; only then was a negative Beilstein test obtained. Isobutyl bromide after 24 hours at 0° and 96 hours at room temperature gave only 37% of the theoretical amount of silver bromide and *ca.* a 40% recovery of isobutyl bromide (which was, however, not quite pure).

The reaction time can be shortened considerably by running the reaction at 0° for 3 hours, then at room temperature for 5 hours and, finally, refluxing until a negative Beilstein test is obtained (*ca.* 4 hours of refluxing for iodides and 18 hours for straight chain bromides). However, the product is then a more complex mixture and the sulfuric acid treatment[7] is necessary to ensure that pure nitroparaffin is obtained; the yields are generally about 15–20% lower.

Spectrophotometric Determination of Nitrite Esters.—Since the lower molecular weight nitrites cannot be separated quantitatively from the reaction solvent it was necessary to devise a method for their determination in ether solution. The absorption spectrum of nitrite esters extends further into the visible than that of any other component of the reaction mixture; at 410 mμ the nitroparaffins, alkyl nitrates, alkyl halides, alcohols and carbonyl compounds do not interfere and, therefore, photometric readings were taken at this wave length on the ether solutions obtained by filtering out the silver salts. The amounts of each nitrite were determined from a calibration curve set up by using known concentrations of that particular alkyl nitrite. The accuracy of the method as checked by means of known mixtures of nitrite and nitroparaffin appears to be good to within 2%. Furthermore, the spectrophotometric technique was applied in the *n*-octyl iodide case. Here the amount of nitrite ester found spectrophotometrically was 14% while, upon rectification, 11% of pure 1-octyl nitrite was isolated.

The primary nitrite esters needed as reference compounds were synthesized by the excellent procedure of Chretien and Longi[19] in which a 40% aqueous solution of $Al_2(SO_4)_3 \cdot 18H_2O$ is added to a cold mixture of saturated aqueous sodium nitrite and the alcohol. After a few hours yields ranging from 70–80% were obtained in all cases (*cf.* Table IV).

TABLE IV

ALKYL NITRITES

Nitrite	B.p. °C.	Mm.	$n^{20}D$	Lit. value B.p. °C.	Mm.	$n^{20}D$	Ref.
n-Butyl	78		1.3762	75		1.3760	*b*
n-Hexyl	64	76	1.3990	50	48	1.3977/23°	*c*
n-Heptyl	41	5	1.4063	58	20	1.4060	*d*
n-Octyl	56	9	1.4127	55	8	1.4129	*e*
Isobutyl	66[a]		1.3702[a]	67		1.3715/22°	*f*
Isoamyl	51	115	1.3870	99		1.3871	*g*

[a] Isobutyl nitrite prepared from isobutyl alcohol and nitrosyl chloride has identical b.p. and $n^{20}D$. [b] W. A. Noyes, THIS JOURNAL, **55**, 3883 (1933). [c] L. M. Soffer, E. W. Parrotta and J. D. Domenico, *ibid.*, **74**, 5301 (1952). [d] Ref. 10. [e] J. C. Krantz, U. S. Patent 2,161,358; *C.A.*, **33**, 7495 (1939). [f] J. W. Brühl, *Z. physik. Chem.*, 16, 214 (1895). [g] Ref. 19.

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(19) A. Chretien and Y. Longi, *Compt. rend.*, **220**, 746 (1945).

WEST LAFAYETTE, INDIANA

NOTES

Some Derivatives of 8-Methylquinoline[1]

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This investigation was conducted as part of a general study concerned with the synthesis and establishment of molecular structures of various previously unreported derivatives of quinoline. Although pertinent information pertaining to the chemistry of 6-bromo-8-methylquinoline and 6-chloro-8-methylquinoline[2] has been reported previously, many of the properties of 8-methylquinoline and its derivatives are as yet not recorded.

Since 6-methyl-5-nitroquinoline[3] results from the nitration of 6-methylquinoline and since 5-nitroquinoline is obtained along with 8-nitroquinoline during the nitration of quinoline, it is not surprising that Noelting and Trautmann[4] reported the preparation of 8-methyl-5-nitroquinoline (I) from 8-methylquinoline by direct nitration. It now appears that 2-chloro-8-methyl-5-nitroquinoline (VI) (m.p. 118–119°) also results from the nitration of 2-chloro-8-methylquinoline (III), but the product differs from that (m.p. 232°) described by Fischer[5] as resulting from the nitration of III. Furthermore Fischer[5] reported that the reduction of his mononitro derivative of III gave a product melting at 148° and possessing amine characteristics; whereas the substance obtained by us on reduction of VI with hydrogen in the presence of Raney nickel melts at 109–110°. The structure of VI as obtained by us was verified by an alternate synthesis from I *via* 1,8-dimethyl-5-nitro-2-quinolone (V).

The acid-catalyzed hydrolysis of VI gave the corresponding 2-hydroxyquinoline; but when 2-hydroxy-8-methylquinoline (IV) was nitrated, a mixture of products resulted from which only a small quantity of 2-hydroxy-8-methyl-5-nitroquinoline (VII) could be isolated. Some 20–30% of the mixture was shown to be 2-hydroxy-8-methyl-6-nitroquinoline (IX). The identity of IX was established by an unambiguous synthesis from 8-methyl-6-nitroquinoline *via* 1,8-dimethyl-6-nitro-2-quinolone and 2-chloro-8-methyl-6-nitroquinoline (VIII).

Hydrogen in the presence of Raney nickel reduces I, VI and VII to the corresponding amines. These amines were converted into arsonic acids, acetamido and benzamido derivatives by resorting to conditions previously reported for effecting such changes.[6]

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(1) Presented in part before the Southeastern Regional Meeting of The American Chemical Society, Wilson Dam, Alabama, October, 1951. Condensed in part from a thesis presented by William E. Blankenstein to the Graduate School of the Alabama Polytechnic Institute in partial fulfillment of the requirements for the degree of Master of Science.

(2) T. A. Irving, J. L. Greene, Jr., J. G. Peterson and J. D. Capps, THIS JOURNAL, **72**, 4069 (1950).

(3) M. T. Bogert and H. L. Fisher, *ibid.*, **34**, 1570 (1912).

(4) E. Noelting and E. Trautmann, *Ber.*, **23**, 3654 (1890).

(5) O. Fischer, *ibid.*, **35**, 3674 (1902).

(6) H. Diaz de Arce, J. L. Greene, Jr., and J. D. Capps, THIS JOURNAL, **72**, 2971 (1950).